AD-A130 817 STRUCTURAL EFFECTS ON HYDROGEN BONDING PROPERTIES OF NITRO COMPOUNDS(U) CALIFORNIA UNIV IRVINE DEPT OF CHEMISTRY R W TAFT MAR 83 N60921-82-C-0039 1/1

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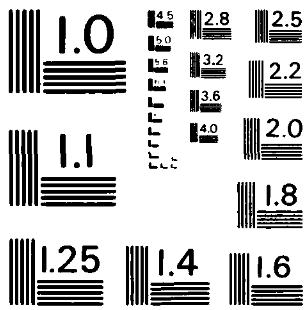

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Values of x, the hydrogen bond donor ability of pure protonic solvents, have been obtained for 18 important solvents including nitromethane. The order of x values for C-H acidic solvents is $(CH_3)_2CO < CH_3CN < CH_3NO_2 < CH_2Cl_2 < CHCl_3$.

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Final Report for Contract N60921-82-C0039
with Naval Surface Weapons Laboratory

Professor R.W. Taft

Attn: Dr. M.S. Kamlet

Values of α, the hydrogen-bond donor ability of pure protonic solvents[1], have been obtained for 18 important solvents (cf. Table A). These values were calculated from 25 data sets which involve a significant number of both non-protonic and protonic solvents and for which the solute measurement is relatively sensitive to the solvent hydrogen bond donor ability. The individual α_i values of Table A were calculated from the correlation equation[1], $XYZ=c+s\pi^*+a\alpha$ expressed as: $\alpha_i = \frac{XYZ-c-s\pi^*}{a}$. The values were averaged to give α_{ave} values given in Table A. In Table B are given the various spectroscopic probe measurements XYZ (electronic transitions, C^{13} and P^{31} NMR shifts) used in the 25 correlations, the values of c,s, and a obtained for each correlation equation, as well as the statistical fit parameters. For protonic solvents, the π^* values used were those recently reported[2]. Four iterations of the 25 correlations equations were carried out to obtain the "limiting" values of π_i given in Table A.

The α scale includes structural effects of solvent self-association as well as of inherent molecular hydrogen-bond donor abilities. The results for C-H acidic solvents appear to be the least affected by self-association. The order of α values found for these solvents is $(CH_3)_2CO < CH_3CN < CH_3NO_2 < CH_2Cl_2 < CHCl_3$. These are striking results since the α values reflect approximately the inherent order of molecular hydrogen bond donor abilities of these C-H acids. This order is distinctly different than that for the gas phase acidities:

$CH_2Cl_2 < CHCl_3 < CH_3CN < (CH_3)_2CO < CH_3NO_2$. Consequently, the results are important in establishing different orders of acidity for hydrogen bonding than for proton transfer. For hydrogen-bonding acidities, there appears to be little importance of resonance stabilization of the conjugate base of the C-H acid, but instead inductive electron-withdrawal which increases the positive charge on hydrogen is the dominant effect. For proton transfer acidity, on the other hand, the dominant effect tends to be resonance stabilization of the carbanionic conjugate base.

Also included in this report is a summary of interrelationships between the various solvent property scales. This work was presented in a poster session at the Euchem Conference on Correlation Analysis in Organic Chemistry, Hull, England, July 19-23, 1982.

References

1. M.J. Kamlet, J.L.M. Abboud, and R.W. Taft, Progr. Phys. Org. Chem., 13, 485 (1981).

2. B. Chawla, S.K. Pollack, C.B. Lebrilla, M.J. Kamlet, and R.W. Taft, J. Am. Chem. Soc., 103, 6924 (1981).

A

Table A. α_i Values from Individual Data Sets and α_{ave} Values for Solvents

Data Set / Solvent	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
MeEtCO	.08		.08						.02	.02	.07							
Me_2CO	.10	.07	.06	.05	.15		.04	.01	.04	.05	.09	.10	.12	.10	.08	.10	.15	.16
MeCN	.31	.30	.28		.26	.27	.22	.20	.23	.18	.18	.05	.08	.12	.12			
$MeNO_2$	.24		.17			.18	.33	.19	.33	.32	.28	.11	.17	.12	.20	.32	.36	.20
CH_2Cl_2	.11	.08			.22				.47	.46	.40		.21	.15	.27	.46	.39	.16
$CHCl_3$	.21				.40							.30	.38	.29	.42			
$HCONH_2$	.81	.68	.65	.70	.59	.63		.72	.83	.81	.70	.68	.67	.66	.68	.77	.69	.57
t-BuOH	.50	.60			.74	.67			.59	.59	.63	.88	.73	.84	.77	.71	.64	.72
i-PrOH	.74	.77	.62	.74	.82	.72	.74	.77	.70	.70	.70		.79	.91	.86	.80	.73	.79
n-BuOH	.86	.85	.79	.80	.80		.76		.71	.71								
n-PrOH	.85	.83	.77	.82			.80		.76	.76	.76							
EtOH	.91	.88	.82	.81	.85	.84	.88	.85	.75	.74	.75	.89	.86	.94	.89	.83	.81	.84
$(CH_2OH)_2$	.84	.81		.87	.91	.84	.85		.86	.88	.85	1.04	1.04	.98	.96			
MeOH	1.09	1.02	1.03	.99	.99	1.01	1.01	.95	.84	.82	.87	.94	.93	.97	.93	.95	.96	.92
CH_3CO_2H									1.01	1.05	1.06					1.11	1.04	1.12
H_2O	1.10	1.11	1.24		1.12	1.24	1.11	1.13			1.23		1.17	1.01		1.01	1.02	1.11
CF_3CH_2OH						1.38			1.74	1.75	1.66	1.39	1.45	1.46	1.40	1.63	1.62	1.43
$(CF_3)_2CHOH$		1.97				2.03										1.83	1.97	2.07

Table A (cont) α_i Values from Individual Data Sets and α_{ave} Values for Solvents

Data Set / Solvent	19	20	21	22	23	24	25	α_{ave}	SD	n
MeEtCo		.11	.12	.01	.04	.05	.04	.06	.04	11
Me_2CO	.13	.00	.01		.02	.06	.04	.08	.05	23
MeCN		.13	.07	.10	.16	.28	.19	.19	.08	20
$MeNO_2$	.20	.17	.06	.17	.16	.37	.27	.22	.09	22
CH_2Cl_2	.21	.34	.30	.31	.04	.30	.30	.30	.11	17
$CHCl_3$		.56	.53	.59	.56	.45	.39	.44	.10	11
$HCONH_2$	.61	.75	.88	.77	.92	.56	.78	.71	.09	24
t-BuOH	.79	.60	.68	.61	.65	.33	.61	.68	.09	20
i-PrOH	.81							.76	.07	18
n-BuOH								.79	.06	8
n-PrOH		.74	.76	.78	.77	.57	.57	.78	.03	12
EtOH	.87	.81	.80	.79	.77	1.15	1.12	.83	.05	23
$(CH_2OH)_2$								.90	.08	13
MeOH	.92	.87	.79	.90	.85	.82	.69	.93	.08	24
CH_3CO_2H	1.22	1.16	.96	1.24	1.30			1.12	.11	11
H_2O	1.12	1.24	1.32	1.43	1.28	1.15	1.20	1.17	.11	20
CF_3CH_2OH	1.44	1.47	1.39	1.45	1.40	1.51	1.62	1.51	.12	18
$(CF_3)_2CHOH$	1.93	1.94	2.06	1.77	1.88	2.11	1.92	1.96	.10	12

Table B Data Sets Used to Define α Values by Correlation Eqns, $XYZ = c + s\pi + a\alpha$

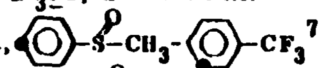
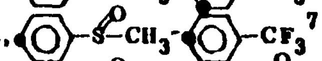
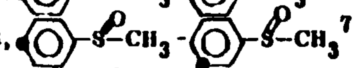
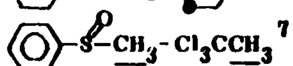
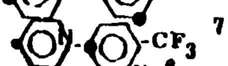
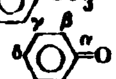
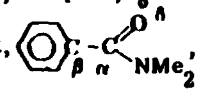
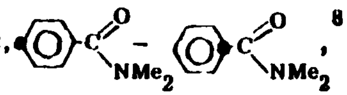
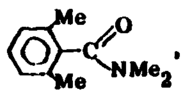
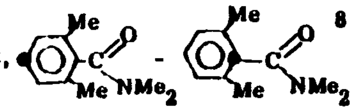
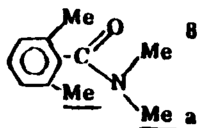
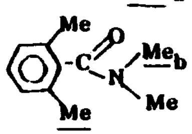
Property	n	c	s	a	a/s	SEs[1]	SEa[2]	R[3]	SEE%[4]	SEE[5]	Excluded
1. $E_T(30)$ (cf. Fig. 47)[6]	27	30.58	14.31	14.97	1.05	1.06	0.82	.984	4.9	1.58	CF_3CH_2OH
2. E_T(cf. Fig. 53).[6] Kosower's Z	16	51.25	18.29	21.01	1.15	2.41	0.99	.986	4.8	1.94	HOAc
3. E_T (cf. Fig. 54)[6]	14	40.23	8.01	9.09	1.14	1.03	0.51	.985	5.3	.76	t-BuOH, dioxane
4. E_T (cf. Fig. 55)[6]	11	61.11	4.34	8.80	2.03	0.44	0.23	.997	2.9	.27	
5. E_T (cf. Fig. 56)[6]	17	79.84	1.68	5.10	3.00	0.32	0.23	.989	4.9	.37	HOAc, $CHCl_3$
6. E_T (cf. Fig. 57)[6]	17	67.61	7.31	6.62	0.91	0.58	0.26	.993	3.4	.60	
7. ν_{max} (cf. Fig. 49a)[6]	13	14.11	0.89	1.60	1.70	0.10	0.06	.994	3.3	.08	
8. P^{31} Shift Et_3PO, Gutmann's AN	17	0.63	16.17	32.47	2.01	1.21	0.85	.996	2.5	1.36	HOAc
9. C^{13} Shift,  [7]	25	1.38	0.01	1.36	226.	0.10	0.06	.981	5.1	.13	CCl_4, $CHCl_3$, $(CF_3)_2CHOH$
10. C^{13} Shift,  [7]	26	- 1.37	- 0.51	1.35	- 2.64	0.09	0.06	.981	4.9	.12	$CHCl_3$, $(CF_3)_2CHOH$
11. C^{13} Shift,  [7]	25	1.05	0.36	0.75	2.06	0.04	0.02	.993	3.2	.05	CH_2Cl_2, $CHCl_3$, $(CF_3)_2CHOH$
12. C^{13} Shift,  [7]	15	- 3.83	- 0.28	- 1.31	4.70	0.13	0.08	.981	6.8	.14	
13. C^{13} Shift,  [7]	20	11.65	0.44	0.98	2.20	0.07	0.04	.989	4.6	.08	HOAc, $(CF_3)_2CHOH$
14. C^{13} Shift,  [7]	20	15.31	- 1.33	- 2.95	2.22	0.27	0.18	.979	6.1	.34	HOAc, $(CF_3)_2CHOH$
15. C^{13} Shift,  [7]	19	3.35	0.00	2.02	-	0.11	0.07	.990	4.6	.13	HOAc, $(CF_3)_2CHOH$
16. C^{13} Shift, Tropone  , δ^{α}_{H} [7]	17	57.66	1.49	2.75	1.84	0.22	0.11	.992	4.0	.25	
17. C^{13} Shift, Tropone, δ^{α}_{β} [7]	17	43.01	2.86	3.42	1.19	0.24	0.11	.994	3.1	.27	
18. C^{13} Shift, Tropone, δ^{β}_{γ} [7]	17	9.25	- 3.96	- 3.91	0.99	0.28	0.13	.995	2.9	.31	
19. C^{13} Shift, Tropone, δ^{γ}_{δ} [7]	17	0.27	1.20	1.35	1.12	0.08	0.04	.996	2.7	.09	
20. C^{13} Shift,  , δ^{α}_{β} [8]	21	32.58	0.73	4.01	5.5	0.23	0.11	.994	3.1	.26	
21. C^{13} Shift,  [8]	21	- 8.52	0.36	2.38	6.6	0.27	0.13	.980	5.7	.30	

Table B (cont)

Property	n	c	s	a	a/s	SEs[1]	SEa[2]	R[3]	SEE%[4]	SEE[5]	Excluded
22. C^{13} Shift,  [8]	21	31.52	1.18	4.23	3.6	0.42	0.20	.984	5.8	.47	$(CH_3)_2CO$
23. C^{13} Shift,  [8]	21	~10.25	0.40	2.63	6.5	0.30	0.14	.979	6.4	.33	CH_2Cl_2
24. C^{13} Shift,  [8]	20	17.81	0.53	1.00	1.90	0.14	0.07	.974	6.2	.15	t-BuOH, n-PrOH, EtOH
25. C^{13} Shift,  [8]	20	14.64	0.34	1.01	3.0	0.11	0.05	.982	5.7	.12	n-PrOH, EtOH, MeOH

(1) Standard Error of s

(2) Standard Error of a

(3) Multiple Correlation Coefficient

(4) Standard Error of Estimate as % of the range of XYZ

(5) Standard Error of Estimate

(6) cf. figures given in Kamlet, Abboud, and Taft, Prog. Phys. Org. Chem., 13, 485 (1981).

(7) B. Chawla, S. K. Pollack, M. Fujio, L. Simanyi, C. Lebrilla, and R. W. Taft, unpublished.

(8) C. W. Fong and H. G. Grant, unpublished.

INTERRELATIONSHIPS BETWEEN THE VARIOUS SOLVENT PROPERTY SCALES

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THE SOLVATOCHROMIC EQUATIONS AND PARAMETERS

1. $XYZ = XYZ_0 + \underline{s}(\pi^* + \underline{d}\delta) + \underline{a}\alpha + \underline{b}\beta + \underline{h}\delta_H + \underline{e}\xi$

π^* IS A SCALE OF SOLVENT DIPOLARITY/POLARIZABILITY.

α IS A SCALE OF SOLVENT HYDROGEN BOND DONOR (HBD) ACIDITY.

β IS A SCALE OF SOLVENT HYDROGEN BOND ACCEPTOR (HBA) BASICITY.

δ IS A "POLARIZABILITY CORRECTION FACTOR" EQUAL TO 0.0 FOR NON-CHLORINATED ALIPHATIC SOLVENTS, 0.5 FOR POLYCHLORINATED ALIPHATICS AND 1.0 FOR AROMATIC SOLVENTS

δ_H, THE HILDEBRAND SOLUBILITY PARAMETER, IS A MEASURE OF SOLVENT-SOLVENT INTERACTIONS WHICH ARE INTERRUPTED IN CREATING A CAVITY FOR THE SOLUTE.

ξ IS A COORDINATE COVALENCY PARAMETER, EQUAL TO -0.20 FOR P=O BASES, 0.0 FOR C=O, S=O AND N=O BASES, 0.2 FOR SINGLE BONDED OXYGEN BASES, 0.6 FOR PYRIDINES, AND 1.0 FOR ALKYLAMINE BASES.

THE $\underline{s}$, $\underline{d}$, $\underline{a}$, $\underline{b}$, AND $\underline{h}$ COEFFICIENTS MEASURE THE RELATIVE SUSCEPTIBILITIES OF XYZ TO THE INDICATED SOLVENT PROPERTIES. THE $\underline{d}$ TERM IS NIL FOR ELECTRONIC SPECTRA WHICH ARE SHIFTED BATHOCHROMICALLY WITH INCREASING SOLVENT DIPOLARITY, AND IS FINITE AND (USUALLY) NEGATIVE FOR OTHER XYZ'S.

BY A JUDICIOUS CHOICE OF SOLVENTS AND REACTANTS OR INDICATORS, IT IS USUALLY POSSIBLE TO REDUCE EQ 1 TO A MORE MANAGEABLE ONE OR TWO TERM EQUATION. FOR EXAMPLE, FOR CERTAIN BASICITY DEPENDENT PROPERTIES,

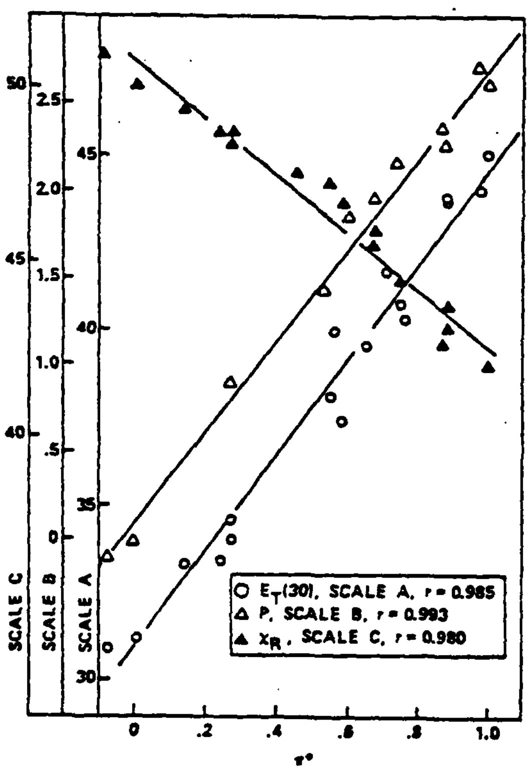
2. $XYZ = XYZ_0 + \underline{b}\beta + \underline{e}\xi$

XYZ IN EQ 1 IS, FOR EXAMPLE, THE LOGARITHM OF A RATE OR EQUILIBRIUM CONSTANT, A FLUORESCENCE LIFETIME, OR A GLC PARTITION COEFFICIENT, A POSITION OR INTENSITY OF MAXIMAL ABSORPTION IN AN NMR, ESR, IR, OR UV/VISIBLE SPECTRUM, AN NMR COUPLING CONSTANT, OR A FREE ENERGY OF SOLUTION OR OF TRANSFER BETWEEN SOLVENTS OF A DIPOLAR SOLUTE.

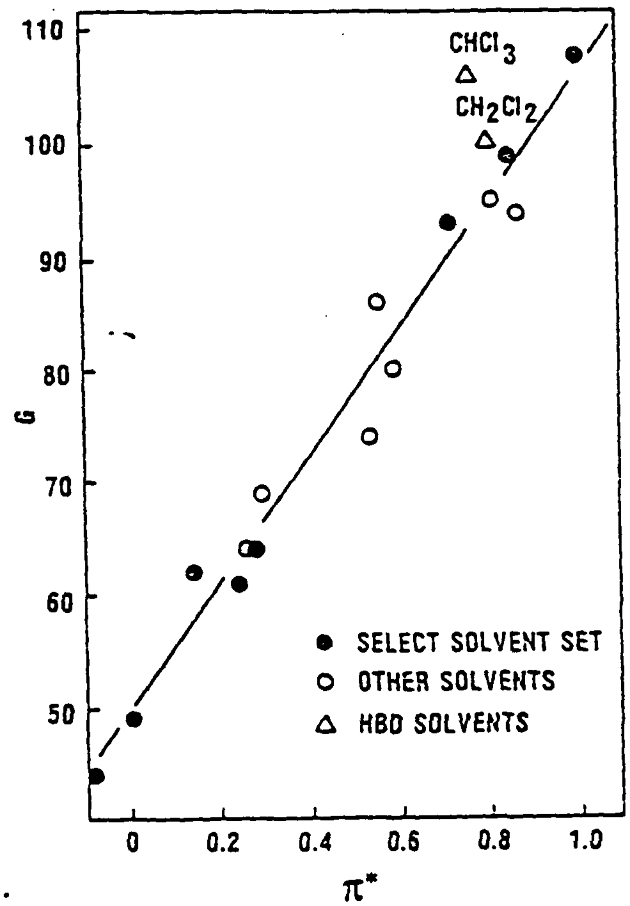
XYZ IN EQ 2 IS, FOR EXAMPLE, AN IR FREQUENCY SHIFT (FREE MINUS HYDROGEN BONDED), AN ENTHALPY OF FORMATION OF A HYDROGEN BONDED OR LEWIS ACID/BASE COMPLEX, OR THE FREE ENERGY OF TRANSFER OF A PROTON TO AQUEOUS BASE FROM AQUEOUS NH_4^+ (THE LATTER QUANTITY BEING LINEAR WITH pK_A).

TABLE II. CORRELATION COEFFICIENTS FOR LINEAR REGRESSION EQUATIONS WITH π^* (SELECT SOLVENTS).

SOLVENT SCALE OR PROPERTY	R	N
DIPOLE MOMENT, μ	0.985	23
REICHARDT AND DIMROTH'S $E_T(30)$, UV/VIS BETAINE	0.987	12
BROOKER'S χ_R, UV/VIS MEROCYANINE	0.987	16
LASSAU AND JUNGERS' LOG K(MEI + PR_3N)	0.985	13
WALTHER'S E_K, UV/VIS MOLYBDENUM COMPLEX	0.977	9
NAPIER AND KNAUER'S A_N, ESR NITROXIDE	0.978	6
ALLERHAND AND SCHLEYER'S G, IR SHIFTS	0.993	8
TAFT'S P, ^{19}F-NMR 4-F-C_6H_4-N=O	0.989	12
BROWNSTEIN'S S (EXTENSION OF KOSOWER'S Z)	0.981	10
SNYDER'S P, GAS/LIQUID PARTITION COEFFICIENTS	0.991	21
GUTMANN'S ACCEPTOR NUMBER, AN, ^{31}P-NMR SHIFTS OF ET_3P=O	0.960	10



DIMROTH'S $E_T(30)$, BROOKER'S χ_R, AND THE NMR-BASED SOLVENT POLARITY PARAMETER, P, FOR SELECT SOLVENTS PLOTTED AGAINST CORRESPONDING SOLVENT π^* VALUES. SELECT SOLVENT ARE NON-CHLORINATED ALIPHATIC SOLVENTS FOR WHICH π^* IS PROPORTIONAL TO MOLECULAR DIPOLE MOMENT.



Allerhand and Schleyer's G Values Plotted against π^*

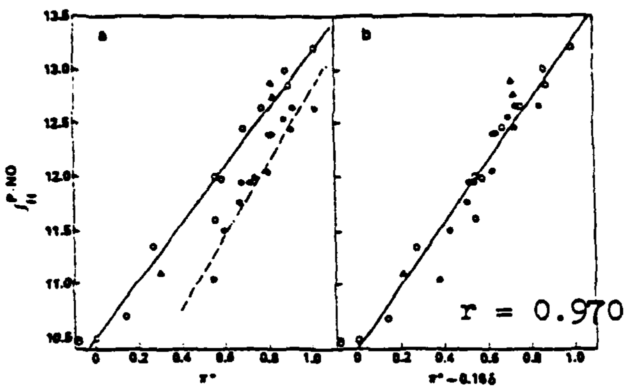


Figure 3. $\int_H^{P\,N=O}$ for *p*-fluoronitrosobenzene plotted (a) against π^* and (b) against ($\pi^* - 0.16\delta$). Symbols for the solvent families are as in Figure 1.

TAFT'S P PLOTTED AGAINST π^* AND AGAINST (π^* - 0.16δ)

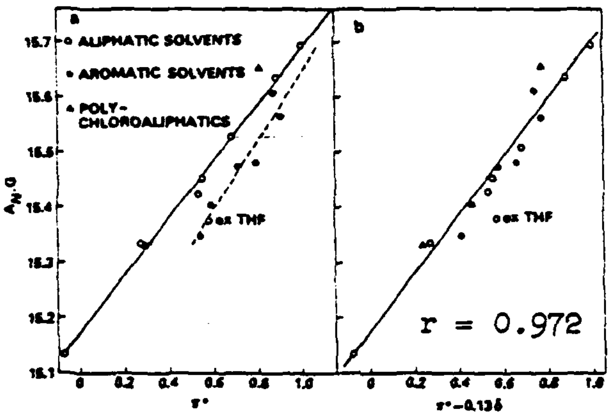


Figure 4. *AN* for di-*tert*-butyl nitroxide plotted (a) against π^* and (b) against ($\pi^* - 0.13\delta$).

NAPIER AND KNAUER'S A_N PLOTTED AGAINST π^* AND AGAINST (π^* - 0.13δ)

1086 *J. Am. Chem. Soc., Vol. 103, No. 5, 1981*

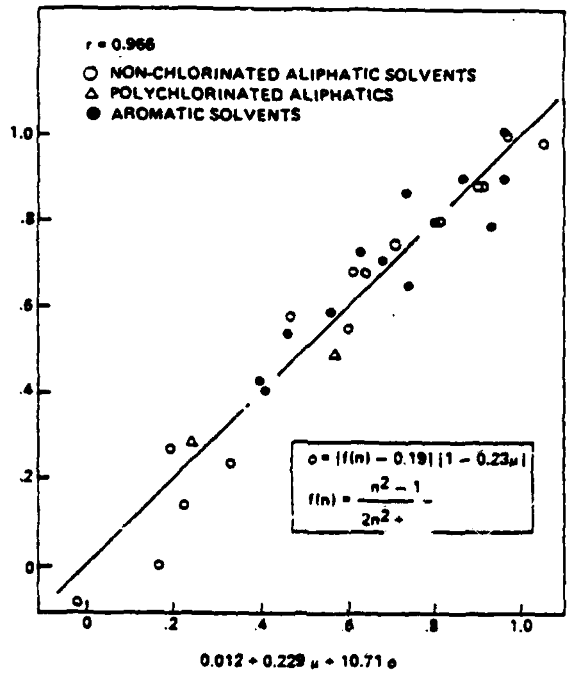


Figure 8. Correlation of π^* with μ and φ.

CORRELATION OF π^* WITH THE SOLVENT DIPOLE MOMENT, μ, AND THE "REDUCING FUNCTION" φ.

THE P/F RATIO IN THE RELATIONSHIP,

$$XYZ = XYZ_0 + F\mu + P\varphi$$

IS LINEAR WITH THE D TERM IN (π^* + Dδ), WITH THE D TERM BECOMING INCREASINGLY NEGATIVE AS THE POLARIZABILITY CONTRIBUTION BECOMES LESS IMPORTANT.

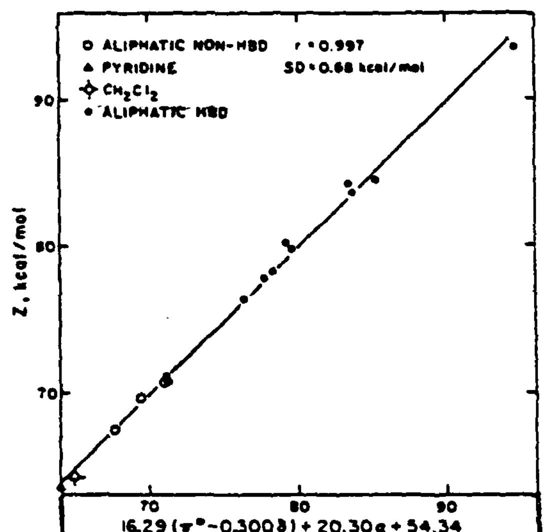
HBD Solvents. Correlations with π^* and α.

When the set of solvents considered includes also protonic solvents, effects of solvent HBD (hydrogen bond donor) acidity must also be included in the solvatochromic equations. Multiple linear regression equations in π^* and α or $(\pi^* + d\delta)$ and α show that the earlier solvent property scales, represented as measures of either solvent polarity (ionizing power) or solvent electrophilicity (acidity) are, in fact, measures of linear combinations of both properties.

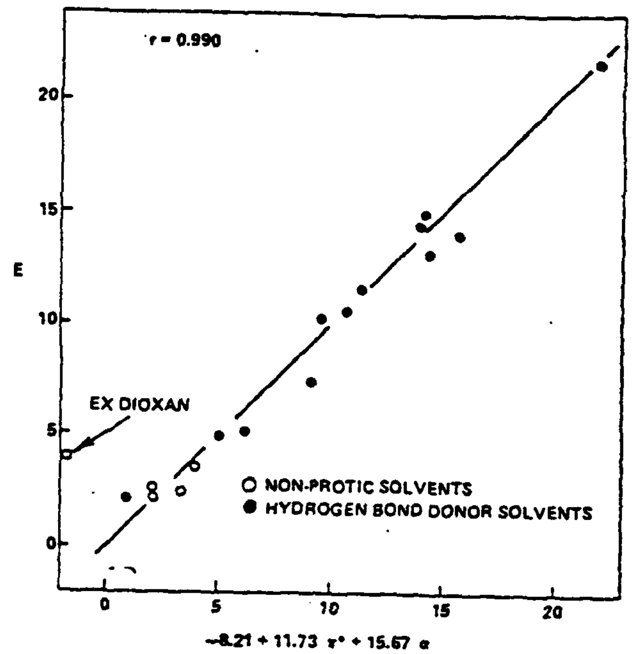
Thus, for Reichardt and Dimroth's betaine,

$$\underline{E_T(30)} = 30.3 + 14.6(\pi^* - 0.23\delta) + 16.4\alpha, \quad N = 44,\ R = 0.993$$

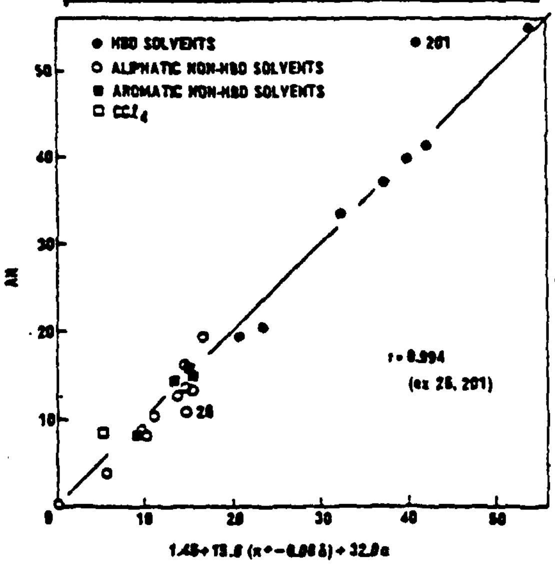
Similarly,



Kosower's Z as function of $(\pi^* + d\delta)$ and α.

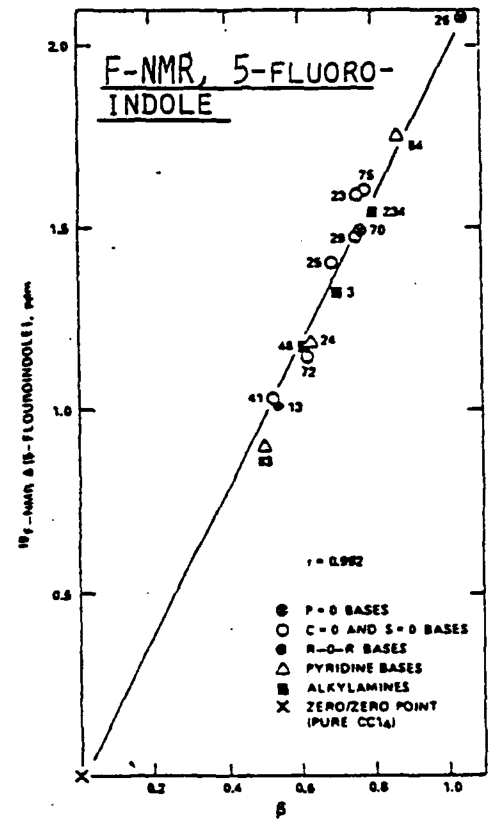


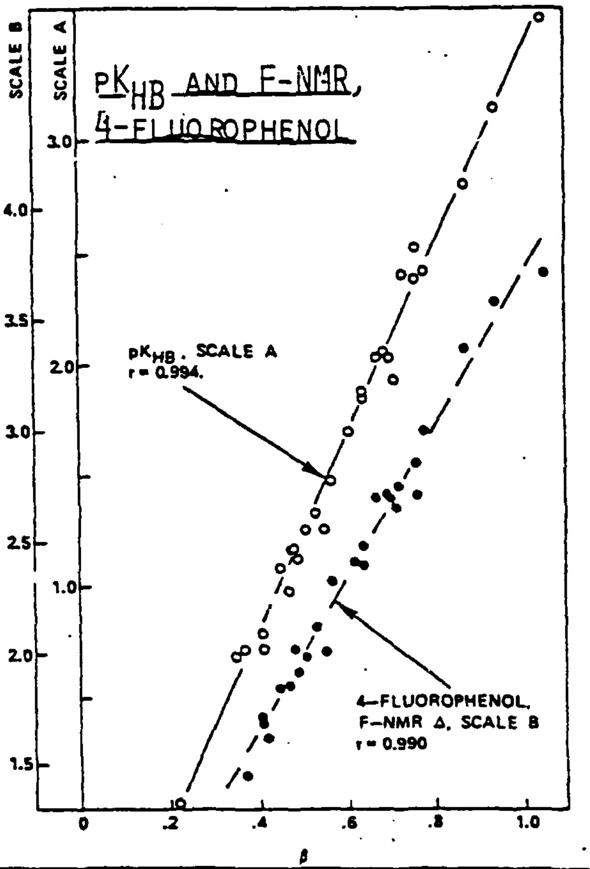
KOPPEL AND PALM'S ELECTROPHILICITY PARAMETER, E, AS A COMBINED FUNCTION OF π^* AND α.



Gutmann's Acceptor Number (AN) as a function of $(\pi^* + d\delta)$ and α.

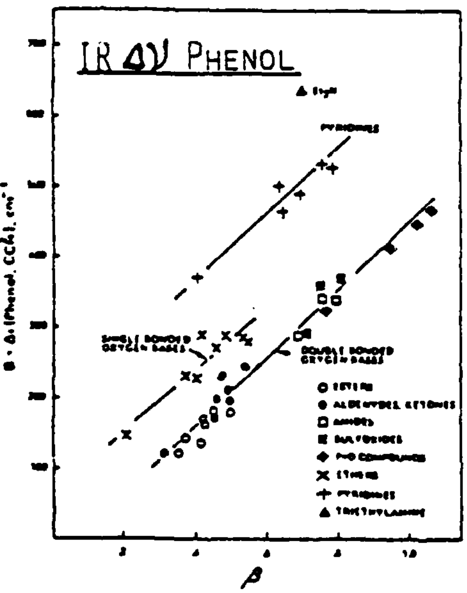
EXAMPLES OF FI CORRELATIONS

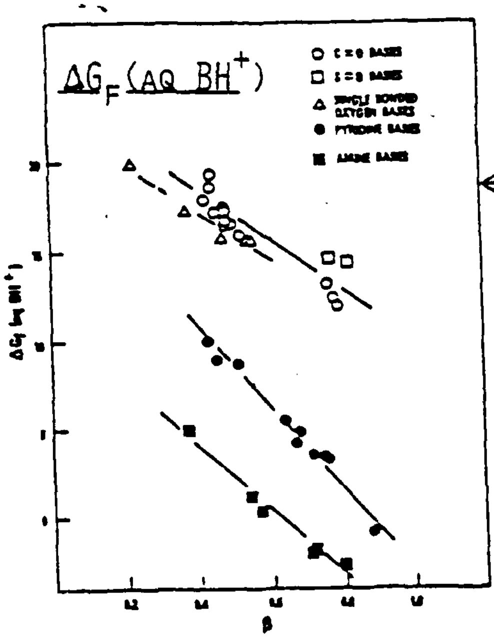




EXAMPLES OF FD CORRELATIONS

BASIS FOR KOPPEL AND PALM'S B SCALE





ΔG$_F$ (AQ BH
IS LINEAR
WITH PK$_{A-}$

Table I. Correlations of Basicity Dependent Properties with E_B/C_B and β/ξ.

	$XYZ = XYZ_o + E_AE_B + C_AC_B$			$XYZ = XYZ_o + b\beta + e\xi$			
Family Independent Properties	n	C_A/E_A	r	n	e/b	r	r'[a]
1. $-\Delta\Delta\nu_{max}$, 3,5-$(NO_2)_2$-φ-NH_2 in pure base	14	0.027	0.926	14	-0.035	0.995	0.995
2. ΔG_f, 4-F-φ-OH:HBA in CCl_4	14	0.044	0.891	14	-0.026	0.982	0.982
3. ^{19}F-NMR Δ, 5-fluoroindole:HBA in CCl_4	8	0.015	0.951	14	-0.010	0.983	0.977
average			0.922			0.987	0.986
Family Dependent Properties							
4. ΔH_f, n-BuOH:HBA in CCl_4 or C_6H_{12}	9	0.060	0.984	14	0.225	0.982	0.955
5. ΔH_f, 4-F-φ-OH:HBA in pure base	13	0.076	0.968	23	0.244	0.974[b]	0.984
5a. " " in CCl_4	8	0.058	0.973[c]	23	0.310	0.966[d]	0.973[c]
6. ΔH_f, φ-OH in CCl_4 or C_6H_{12}	17	0.112	0.986	17	0.444	0.967	0.967
7. Log k/k_o, catalyzed n-butylaminolysis of 4-NO_2-φ-O-CO-CF_3 in $ClCH_2CH_2Cl$	5	0.169	0.989	8	0.460	0.985[f]	0.998
8. ΔH_f, CF_3CH_2OH:HBA in CCl_4 or C_6H_{12}	10	0.106	0.992	10	0.485	0.984	0.984
9. $\Delta\nu$(O-D), MeOD:HBA in pure base	13	0.122	0.987	25	0.570	0.988	0.983
10. ΔG_f, I_2:HBA in heptane	15	0.175	0.950	34	0.570	0.982	0.968
11. ΔH_f, BF_3:HBA in CH_2Cl_2	13	0.110	0.953	34	0.577	0.978	0.973
12. $\Delta\nu$(O-H), φ-OH:HBA in CCl_4	17	0.129	0.991	43	0.611	0.989	0.989
13. ^{19}F-NMR Δ, 4-F-φ-$SO_3^-BH^+$ ion pair in CH_2Cl_2				10	0.642	0.953	
14. ΔH_f, 4-F-φ-$SO_3^-BH^+$ ion pair in CH_2Cl_2				10	0.744	0.993	
15. $\Delta\nu$(C-I), I-CN:HBA in CCl_4	11	0.217	0.994	25	0.787	0.981	0.989
16. ΔH_f, I_2:HBA in heptane	10	0.253	0.995	23	0.859	0.989	0.989
17. ΔG_f, Aq BH^+ in water	14	0.210	0.978	36	0.859	0.992	0.986
average			0.980			0.980	0.983

a) r' is β/ξ correlation coefficient for same data set as was used with E/C. b) ex diphenyl ether and 1,2-dimethoxyethane; if these are included r = 0.969. c) Ex tetramethylurea; if included r = 0.813. d) Ex tetramethylurea and triphenyl phosphate; if the latter is included r = 0.926. e) Ex 4-dimethylaminopyridine and quinuclidine; if included r = 0.971. f) Ex 4-dimethylaminopyridine; if included r = 0.973.

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